SYNTHESIS OF NANOCELLULOSE FROM RUBBERWOOD FIBERS

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ABSTRACT

This research deals with the synthesis of nanocellulose from rubberwood (*Hevea brasiliensis*) fibers via ultrasonication combined with enzymatic and chemical pretreatments. Cellulose nanofibers were separated from rubberwood fibers in three distinct stages. Initially, rubberwood fibers were subjected to a series of enzymatic and chemical pre-treatments to eliminate lignin and hemicellulose. The obtained cellulose fibers were then mechanically separated into nanofibers using ultrasonication. The diameter distributions of the resulting nanofibers were dependent on the output power of ultrasonic treatment. The extent of dispersion improved significantly with increasing output power of ultrasonic treatment. Microscopy study showed that the diameters of the nanofibers isolated ranged from 8.7 to 20 μm. The effectiveness of laccase and xylanase enzymes was also studied. The results obtained from FTIR and thermogravimetric analyses indicated that there were consistencies between the studied enzymes to the thermal stability or chemical structure. FTIR spectroscopy confirmed that the prominent peaks indicating that most of the lignin and hemicellulose were removed during the step-wise chemical treatment were present in the spectrum. FTIR spectroscopy suggested that the spectrum of cellulose nanofibers obtained under different ultrasonic output powers and cellulose fibers were similar, signifying that the molecular structure of cellulose were unaffected by the ultrasonic treatment. Results from TGA analysis revealed that the thermal properties of cellulose nanofibers were enhanced and the thermal degradation temperature increased to proximately 310 °C as compared to 240 °C of the untreated rubberwood fibers. Results from this work may be potentially applied in various fields such as bio-nanocomposites, filtration media packaging, tissue engineering scaffolds, and so on.

ABSTRAK

Kajian ini berkaitan dengan sintesis nanoselulosa daripada gentian kayu getah (Hevea brasiliensis) penggabungan ultrasonikasi dengan pra-rawatan menggunakan enzim serta kimia. Pemisahan nanoselulosa daripada gentian kayu getah merangkumi tiga peringkat yang berbeza. Pada mulanya, gentian kayu getah melalui satu siri pra-rawatan enzim dan kimia untuk menghapuskan *lignin* dan hemiselulosa. Gentian selulosa yang diperolehi telah diuraikan kepada gentian nano menggunakan rawatan ultrasonikasi. Taburan diameter nanofibers terhasil bergantung pada kuasa keluaran rawatan ultrasonik. Tahap penyebaran meningkat dengan ketara dengan meningkatkan kuasa output rawatan ultrasonik. Kajian mikroskopi menunjukkan bahawa diameter nanofibers diasingkan antara 8.7 ke 20 μm. Keberkesanan enzim *laccase* dan *xylanase* turut dikaji. Keputusan yang diperolehi daripada analisis FTIR dan termogravimetri adalah konsisten antara enzim dikaji untuk kestabilan haba atau struktur kimia. Spektroskopi FTIR mengesahkan kewujudan puncak terkemuka dalam spektrum yang dapat membuktikan bahawa sebahagian besar lignin dan hemiselulosa telah dikeluarkan semasa rawatan kimia. Spektroskopi FTIR mencadangkan bahawa spektrum gentian nanoselulosa yang diperoleh di bawah kuasa ultrasonik yang berbeza adalah sama dengan gentian selulosa. Ini menandakan bahawa struktur molekul selulosa tidak terjejas oleh rawatan ultrasonik. Hasil daripada analisis TGA mendedahkan bahawa sifat haba daripada gentian nanoselulosa telah dipertingkatkan dan suhu degradasi haba meningkat kepada hampir 310 °C berbanding dengan 240 °C untuk gentian kayu getah yang tidak dirawat. Hasil kajian ini berpotensi digunakan dalam pelbagai bidang seperti bio-nanokomposit, penapisan pembungkusan media, perancah kejuruteraan tisu, dan sebagainya.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

BC	Bacterial Cellulose
DP	Degree of polymerization
FE-SEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
GDP	Gross Domestic Product
L	Lumen
ML	Middle lamella
P	Primary wall
S	Secondary wall
T	Tertiary wall
TGA	Thermogravimetric Analysis

LIST OF SYMBOLS AND UNITS

cm^{-1}	reciprocal centimeter
nm	nanometer
rpm	revolution per minute
wt%	percentage in weight
°C	degree Celcius

Greek

μ	micron

1 INTRODUCTION

1.1 Background of study

Cellulose is one of the most ubiquitous and abundant polymers on the planet. It is the world's most natural renewable biodegradable polymer and has been estimated that globally around 10^{12} tonnes are synthesized and also destroyed each year (Hon, 1994). Cellulose is a classic example where the reinforcing elements exist as whisker-like microfibrils that are biosynthesized and deposited in a continuous manner (Itoh & Brown, 1984). Cellulose is widely distributed in wood, consisting of up to 50% cellulose, is the most important raw material source for cellulose (Klemm et al., 2011). The development of low-cost, sustainable and renewable resources is critical to meet the growing environmental concerns and energy demands. Regardless of its source, cellulose consists of a linear homopolysaccharide composed of β-d-glucopyranose units linked together by β-1-4-linkages. The repeat unit is a dimer of glucose, known as cellobiose. Each monomer has three hydroxyl groups and it is therefore obvious that these hydroxyl groups and their ability to form hydrogen bonds play a major role in directing the crystalline packing and also governing the physical properties of cellulose (Maya Jacob & Sabu, 2008).

There is a significant variation of the lignin, hemicellulose and cellulose contents relying upon whether it is derived from wood, cotton, agricultural products and etc. Wood contains from about 20% to 30% lignin, removal of which is a main objective of bleaching processes. It is an amorphous three-dimensional polymer with phenyl propane units as the predominant building blocks. Lignin is the most complex natural polymer with acid insoluble character. Hence, bleaching approach was used for maximal elimination of remaining cementing materials from wood fibers. From a technological point of view, lignin content evaluation in the biomass is important to optimize the chemical and mechanical pre-treatment parameters necessary to produce a pure cellulose pulp. Indeed lignin is the hardest chemical component to be removed from lignocellulosic biomass. The term hemicellulose is a collective term. It is used to represent a family of water soluble polysaccharides that are found in the plant cell wall and comprises of different composition and structure depending on their source and the extraction method. The most common type of polymers that belongs to the

hemicellulose family of polysaccharides is xylan. Harmsen et al. (2010) also added that important aspects of the structure and composition of hemicellulose are the lack of crystalline structure mainly due to the highly branched structure. Thus, hemicellulose can be conveniently hydrolyzed in mild acidic or alkaline conditions. The presence of acid greatly improves the solubility of hemicellulose in water.

Cellulose is a major structural component of cell walls that provides mechanical strength as well as chemical stability to plants. Cellulose is a relatively hygroscopic (tendency of a substance to absorb moisture from the air) material, absorbing 8 to 14% water under normal atmospheric conditions at 20 °C and 60% relative humidity (Harmsen et al., 2010). Nevertheless, it swells when placed in water due to its insolubility in water. The cellulose fraction is more resistant and therefore requires much rigorous treatment. According to Hubbe et al. (2008), cellulose nanofibers have many advantages when compared with the inorganic fibers. Some of the most relevant benefits being the following such as low density, high biodegradability, renewable sources, non-food agricultural based economy, low abrasivity and low energy consuming per product unit. These advantages of cellulose nanofibers ensures a greater durability of the processing equipment, high specific strength and modulus, high sound attenuation of lignocelluloses based composites and reduced carbon dioxide emission in the environment to name a few.

The term nanocellulose generally refers to cellulosic materials consisting of elementary assemblies of explicit polymer units that have diameters in the order of tens of nanometers. Nanocellulose exhibits elongated crystalline rod like shapes and has very limited flexibility because it does not contain amorphous regions. It is formed by rigid rod like particles with widths and lengths of 5 to 70 nm and between 100 nm and several micrometers respectively. The separation of nanocellulose from cellulose source materials occurs generally in three stages. The first being the pre-treatment of the source material which is rubberwood fibers in this case. In the case of wood, the pre-treatment stage involves the complete or partial removal of matrix materials such as lignin, hemicelluloses and cellulosic fibers. The second stage is a controlled chemical treatment which generally consists of hydrolysis to remove the amorphous regions of the cellulose polymer. For wood and plant source materials, the pre-treatments are similar and consist of techniques that are usually used in pulp and paper industry. In practice, lignin hinders the separation of wood into its component fibers. Thus, delignification of wood fibers is

an essential preparation step to produce nanocellulose. Here, the processes mainly consist of a chemical treatment of wood fibers to depolymerize and eventually solubilize lignin and hemicelluloses. A subsequent bleaching process is carried out with oxidizing agents such as sodium chlorite ($NaClO_2$). All these steps permit the removal of lignin and hemicelluloses while leaving cellulose components intact if optimal conditions are respected. The amorphous domains are preferentially hydrolyzed during hydrolysis whereas crystalline regions have higher resistance to alkali attack (Habibi et al., 2010).

The third stage deals with the mechanical treatment on the purified wood fibers. The synthesis of cellulose nanofibers from cellulose fibers using a modest, low cost and environmentally friendly method is a great challenge. Recently, the ultrasonic technique has been to isolate cellulose nanofibers (Chen et al., 2011; Cheng, Wang, & Han, 2010; Cheng, Wang & Rials, 2009). Ultrasonication is the application of sound energy to physical and chemical systems. Non-conventional chemistry appears to offer important possibilities in the arsenal of environmentally friendly synthetic methods, especially in connection with the emerging concept of 'Green Chemistry' (Anasts & Williamson, 1998). This method helps in the reduction of wastes, the design of non-polluting products and processes as well as an optimal use of materials. With regards to the concerns stated above, it is reasonable to consider the combination of enzymatic and chemical pre-treatments combined with sonochemistry as a tool in the design of original synthetic pathways. The precise morphological characteristics of cellulose nanofibers are usually analyzed by microscopy inclusive of Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM).

1.2 Motivation and statement of problem

Cellulose is one of the most ubiquitous and abundant polymers on the planet. In plants and trees, cellulose acts as a structural reinforcing agent that provides mechanical strength as well as chemical stability to plants. Cellulose is a classic example where the reinforcing elements exist as whisker-like microfibrils that are biosynthesized and deposited in a continuous manner (Itoh & Brown, 1984). As the demands to substitute the less environmentally friendly materials with more sustainable ones are growing as well as new applications for biocomposites are being developed, demands on the performance of composites are also increasing. Technology based on renewable

materials can help support the enormous requirements of growing population in a sustainable fashion. Cellulose, which is the most abundant renewable material on our planet, is thus an appropriate choice to guide humanity towards a truly ecofriendly existence.

A number of studies have been conducted to elucidate the synthesis of highly purified cellulose nanofibers from cellulosic materials via cryocrushing (Chakraborty, Sain, & Kortschot, 2005, 2006), grinding (Abe et al., 2007; Abe, Nakatsubo, & Yano, 2009; Abe & Yano, 2009, 2010; Nogi et al., 2009), high pressure homogenizing (Herrick, Casebier, & Hamilton, 1983; Nakagaito & Yano, 2004, 2005, 2008a, 2008b; Turbak, Snyder, & Sandberg, 1983), chemical treatments (Araki et al., 2000; Elazzouzi-Hafraoui et al., 2007; Liu et al., 2010), biological treatments (Hayashi, Kondo, & Ishihara, 2005; Henriksson et al., 2007; Pääkkö et al., 2007) as well as a combination of two or several of the aforementioned methods. Since cellulose nanofibers are embedded in matrix substances such as hemicellulose and lignin, chemical methods are the most common approach utilized in removing the matrix substances (Fan, Saito, & Isogai, 2008; Ifuku et al., 2009). However, there has been inadequate research for ultrasonic treatment. Due to its environmental benefits and convenience of the operation, ultrasonication has been selected to isolate cellulose nanofibers. Recent work by (Chen et al., 2011) suggested that ultrasonication has insignificant effect on the fiber properties. The application of enzymes in fiber processing has been mainly directed to the degradation or modification of hemicelluloses and lignin while preserving the cellulosic fraction (Janardhnan & Sain, 2006). In addition, past studies were conducted to investigate the use of enzymes in enhancing the bleaching of cellulose fibers. The study repealed that the final brightness of pulp was enhanced with the aid of xylanase (Clark et al., 1991; Senior et al., 1992; Ratto et al., 1993; Suurnäkki et al., 1994; Li et al., 1996; Morkbak & Zimmermann, 1998; Paice et al., 1998; Madlala et al., 2001; Bobu et al., 2003; Chen, Qu, & Yang, 2006). A combination of methods often yields preferable cellulose nanofibers. Hence, this study aims to synthesize nanocellulose from rubberwood fibers via ultrasonication combined with enzyme and chemical pretreatments.

1.3 Research objective

The following is the research objective for this study:

- To synthesize nanocellulose from rubber wood fibers via high-intensity ultrasonication in combination with enzyme and chemical pre-treatments.

1.4 Scope of this research

The following are the scope of this research:

I. Performing a series of treatments on rubberwood fibers which are:
   a) Enzyme pre-treatment using xylanase and laccase enzymes, and
   b) Chemical pre-treatment using acidified sodium chlorite ($NaClO_2$) and potassium hydroxide (KOH).

II. Studying the effect of different enzymes on the purity of cellulosic fibers by varying the enzymes which are:
   a) Laccase, and
   b) Xylanase

III. Studying the effect of ultrasonication on the synthesis of nanocellulose by varying the output powers which are:
   a) 80 W,
   b) 100 W, and
   c) 200 W,

IV. Analyzing and characterization of the nanocellulose obtained by conducting analyses such as:
   a) Scanning Electron Microscopy (FE-SEM),
   b) Fourier Transform Infrared Spectroscopy (FTIR), and
   c) Thermogravimetric Analysis (TGA).

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 1 provides an overview of this research study. Among the content discussed is the introduction of cellulose which will be extracted from rubberwood fibers as one of the main material for the synthesis of nanocellulose. Furthermore, the problem

statement, research objectives as well as the scope of study are also encompassed in this chapter.

Chapter 2 discusses mainly on the literature review concerned with the introduction of the lignocellulosic materials (lignin, hemicellulose and cellulose) along with the treatments which will be applied in this study. Also, all relevant journals, articles and technical paper from past studies will be reviewed and discussed in detailed.

Chapter 3 presents the research methodology. This includes a detailed description on the method used for this research as well as the materials and apparatus needed. In addition, the description on the method used for analysis of sample is also presented.

Chapter 4 covers the complete description of results and discussion. All experimental results obtained are discussed briefly. The detailed discussion on the product quality analysis is evaluated.

Chapter 5 draws together a summary of the thesis and outlines the future work which might be derived from this work as well as appropriate recommendations for improvement.

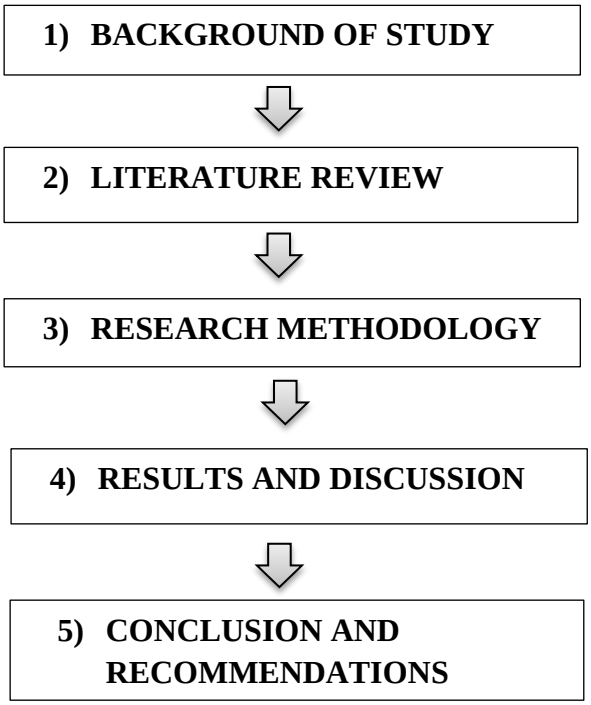

Figure 1-1: The road map for thesis

2 LITERATURE REVIEW

2.1 Overview

This chapter presents a brief introduction on cellulose and also the review of previous studies on the synthesis of nanocellulose from rubberwood fibers using high-intensity ultrasonication in combination with enzymatic and chemical pre-treatments.

2.2 Introduction

Cellulose is one of the most important natural polymers, an almost inexhaustible raw material and can be well thought-out as a key source of sustainable materials on an industrial scale. Cellulose acts as a structural reinforcing agent in plants and trees, whose key function is to provide mechanical strength. Cellulose has been used for millennia from being a basic energy and textile source, ranging to building material and paper. Lately, cellulose has been utilized in biotechnology and has gained considerable interest in medical implementations. The growing significance of bio-based materials have drawn public interest into incorporating renewable resources such as polysaccharides in areas where synthetic fibers and petroleum based polymer were used previously. One of the vast markets for cellulose is focused on novel composite materials by utilizing the natural good mechanical properties of cellulose fibers. For the aforementioned reasons, it is of great importance to know the structure of cellulose and moreover how it interacts with other materials when introduced to diverse environmental conditions. By acquiring knowledge of the chemical nature of the cellulose molecules in addition to its structure and morphology in the solid state, the chemical and physical properties of cellulose can be understood (Krassig, 1996).

In recent years, there has been a remarkable growth in interest in the use of nanocellulose as polymer reinforcement in order to create high-performance biomaterials. The core reason for the appeal of nano-sized cellulose is that material with higher uniformity and fewer defects with enhanced mechanical properties can be acquired by reducing the size of the cellulose fiber (Spence, Habibi, & Dufrense, 2011). Nanocellulose has the benefit of being a sustainable material due to its biodegradability and renewability. Nanocomposites are expected to have improved mechanical, thermal and barrier properties in contrast with conventional composite materials (Siró &

Plackett, 2010; Svagan, Azizi, & Berglund, 2007). There are a widespread variety of possible applications for cellulose nanocomposites, varying from replacement of synthetic materials with more environmentally friendly materials to producing completely new types of biomaterials. At present, cellulose nanocomposites are being considered for use in medical, packaging, automotive, electronics, construction and water treatment applications (Oksman, Mathew, & Sain, 2009).

Wood has had a great significance as a building material for construction, furniture, tools and vehicles throughout the history of humankind. Today, wood is used as raw material for a great variety of products including construction timber, paper products and sports equipment. The enormous abundance of rubberwood has been considered as an attractive starting material for the synthesis of nanocellulose. *Hevea brasiliensis*, or more commonly known as rubberwood, is the largest commodities contributing to the gross domestic product (GDP) of Malaysia (Jonoobi et al., 2011). In addition, rubberwood is a conventional input material for wood-based products. For this study, rubberwood fibers have been chosen to synthesize nanocellulose due to its fine texture, light colour, appreciably high strength and good machining properties.

Wood can be considered nature's composite material since it consists of a cellular structure of cellulose in a matrix of lignin, hemicelluloses and extractives. According to Coulson (2011), there are at least 60 000 different wood species in the world and, depending on the species and growth settings, variability can be found in the characteristics and quantity of wood constituents and cell structure. The main components of wood are cellulose, hemicelluloses, lignin and extractives. The composition of lignocellulose constituents vary from plants to plants and highly depend on its source. There is a significant variation of the lignin and hemicellulose content of lignocellulose depending on whether it is derived from hardwood or softwood. In this case, rubberwood is categorized as hardwood. The amounts of each of these components in softwoods and hardwoods are presented in Table 2-1.

Table 2-1: Chemical components of wood by Smook (1999)

Component	Softwood (%)	Hardwood
Cellulose	42 ± 2	45 ± 2
Hemicellulose	27 ± 2	30 ± 5
Lignin	28 ± 2	20 ± 4
Extractives	3 ± 2	5 ± 3

2.3 Structure of wood cell wall

The structure of a wood cell wall is composed of several layers and it is very complex. The typical cell wall structure is shown in Figure 2-1. The cell wall is made up of middle lamella (ML), primary wall (P), secondary wall (S) with three layers and lumen (L) (cf. Figure 2-1). These layers have different structures and chemical compositions, however, the main difference is in their microfibril arrangements. Microfibrils are cellulose molecules bundled together (Smook, 1999; Ilvessalo-Pfäffli, 1997).

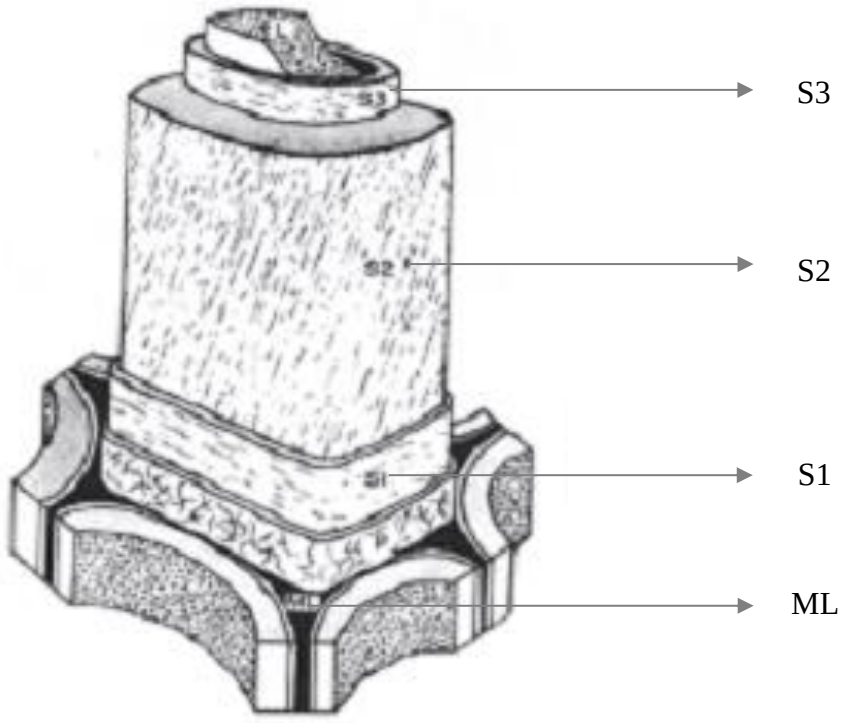

Figure 2-1: Cell wall structure by Côté, Jr. (1967)

The middle lamella (ML) does not actually belong to the cell wall because it separates two neighbouring fibers from each other. ML has high lignin content and it is amorphous. Primary wall (P) is the outermost layer of the cell wall of wood fiber. It is a thin layer consisting mainly of lignin and pectins. The secondary wall (S) has three layers, namely S1, S2 and S3. These layers vary from each other on different microfibril alignments and compositions. S1 is a thin and lignin-rich outer layer, S2 is a thick middle layer and S3 is a thin inner layer. The S2 layer is technically the most valuable for it is rich in cellulose. The inner layer of the secondary wall, S3, also called the tertiary wall (T), is composed mainly of hemicelluloses. In the middle, there is a canal called lumen (L) (Hakkila, 1998; Smook, 1999; Ilvessalo-Pfäffli, 1997).

The morphological hierarchy is defined by elementary fibrils, which are packed into larger units called microfibrils and in turn assembled into fibres (Fengel & Wegener, 1989; Habibi et al., 2010). Elementary fibrils are bundles of cellulose molecules and its diameter is about 3.5 nm. The cell wall of wood fibers consists of repeated crystalline structures resulting from the aggregation of cellulose chains, also known as microfibrils. Within each of these microfibrils, there are regions in which the cellulose chains are arranged in crystalline structures and regions that are amorphous (Moon et al., 2010). It is these crystalline regions, when extracted, will result in nanocellulose. In the crystalline regions the inter- and intra-molecular interactions networks and the molecular orientations can vary, giving rise to cellulose polymorphs or allomorphs. The crystalline regions are stronger and it is much difficult for solvents or reagents to penetrate into them. In nature, cellulose does not occur as an isolated individual molecule. Instead, it is found as assemblies of individual cellulose chain-forming fibres. When the microfibrils or elementary fibrils are separated from the wood cell wall they are called cellulose nanofibers. Ultimately, an elementary fibril can be considered a single cellulose nanofiber (Smook, 1999; Ilvessalo-Pfäffli, 1997; Meier, 1962; Chinga-Carrasco, Yu, & Diserud, 2011). A schematic representation of the structure of a wood cell wall is shown in Figure 2-2.

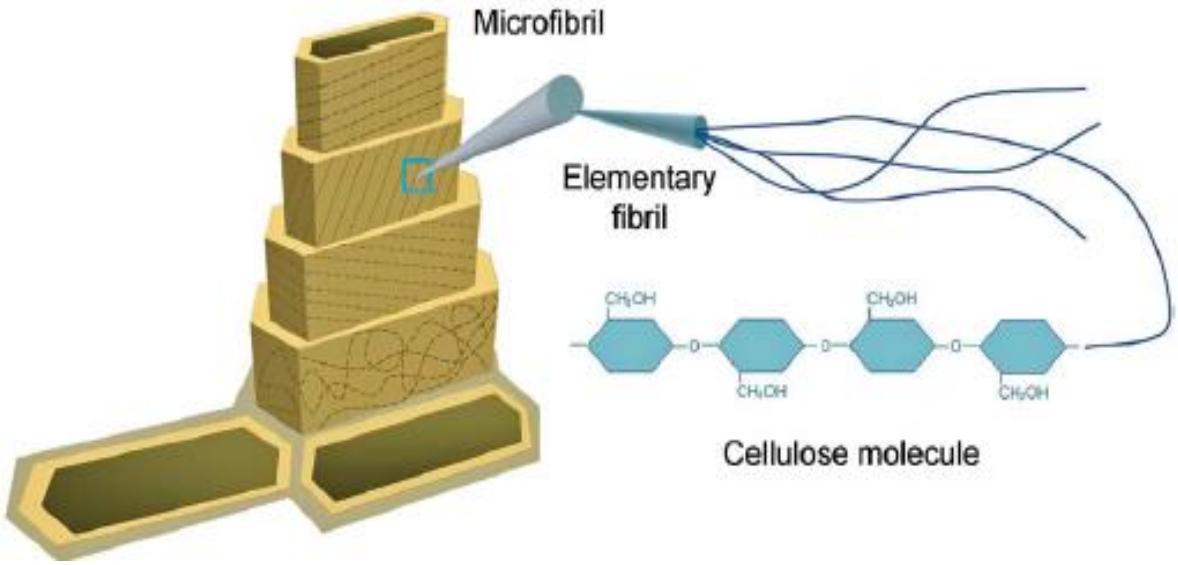

Figure 2-2: Schematic representation of the structure of a wood cell wall by Côté, Jr. (1967)

As it is schematically illustrated in Figure 2-3, microfibrils agglomerate further into larger aggregates. These, along with hemicelluloses and lignin, form the plant cell wall that is the fibre (Eichhorn et al., 2010; Isogai, Saito, & Fukuzumi, 2011).

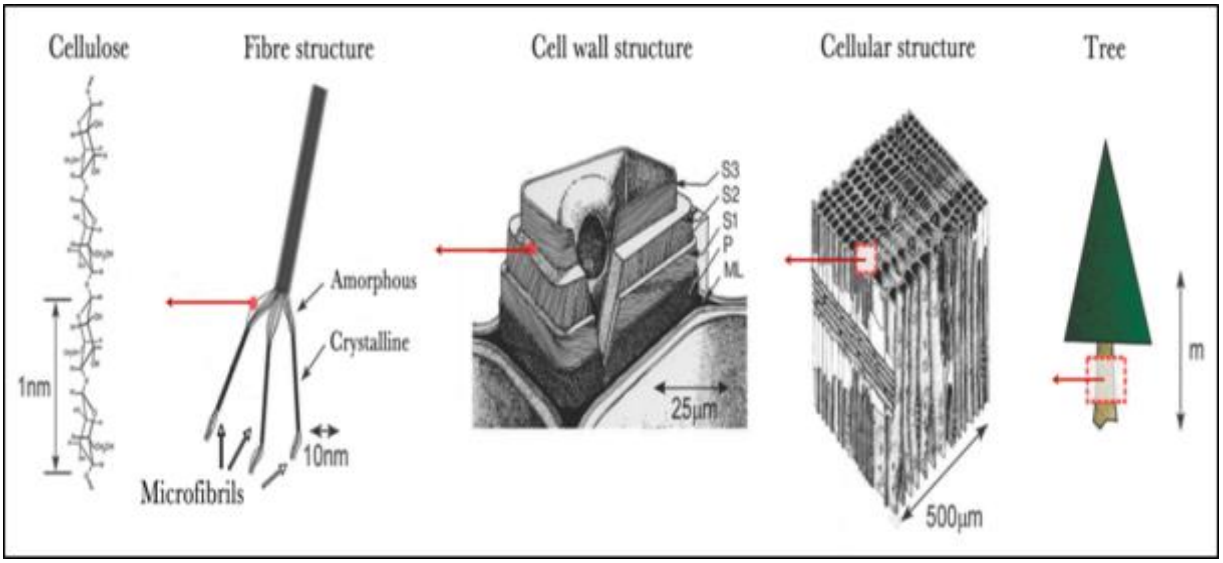

Figure 2-3: Hierarchical structure of wood biomass and the characteristics of cellulose by Moon et al. (2010)

The placement of lignocellulosic materials in a fiber wall can be schematically illustrated in Figure 2-4 below.

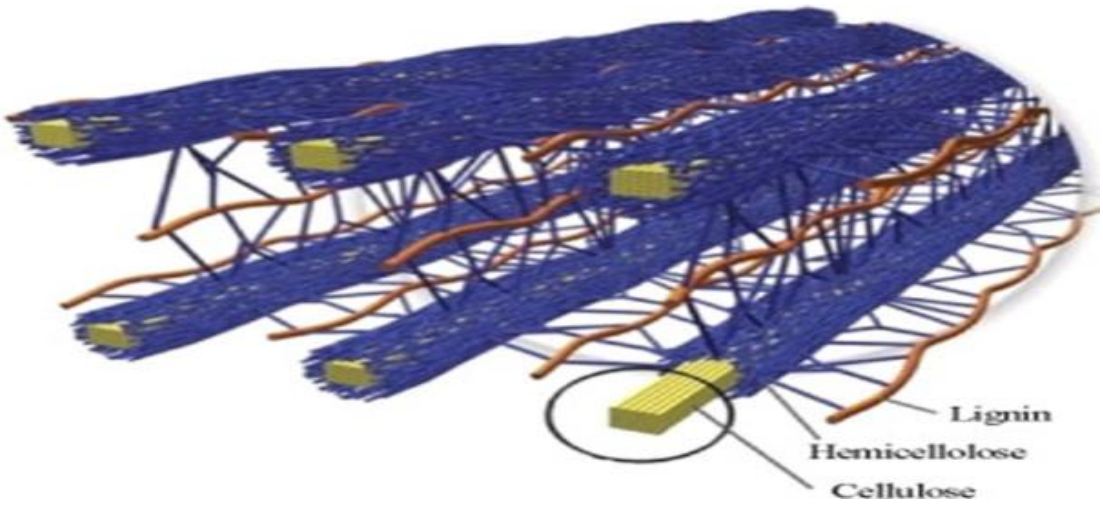

Figure 2-4: Placement of lignocellulosic constituents (lignin, hemicellulose and cellulose) in a fiber wall by Chen et al. (2001)

Cellulose retains the crystalline fibrous structure and it appears to be the core of the complex at the interior of the lignocellulose complex. While hemicellulose is positioned both between the micro- and the macrofibrils of cellulose, lignin provides a structural role of the matrix in which cellulose and hemicellulose is embedded (Faulon, Carlson, & Hatcher, 1994).

Lignin is an amorphous and highly polymerized substance with a very complex structure. It is a three dimensional amorphous polymer which forms a protective layer that grips cellulose and hemicelluloses together. Lignin acts like a physical barrier that limits the availability of the cellulose material. In addition, different kinds of substances, e.g. resin acids, fatty acids and alcohols, are present in wood. These substances are typically called extractives, contributing to wood properties such as color, odor, taste, decay resistance, density and flammability. The name “extractives” comes from the fact that these substances can be removed from the wood by extraction with solvents. (Smook, 1999; Miller, 1999). Besides, lignin is a polymer with acid insoluble character, meaning that the presence of alkali highly improves the solubility of lignin in water.

Hemicelluloses are branched heterogeneous polysaccharides consisting of five different sugars, namely glucose, mannose, galactose, xylose and arabinose. Hemicelluloses have lower molecular weight than cellulose and they have lower degree of polymerization (DP) (Hakkila, 1998). Hemicelluloses tend to degrade and dissolve more easily than cellulose. In addition to that, their amount in pulp is always less than in the original wood. Besides cellulose and hemicelluloses, wood contains lignin and extractives. The term hemicellulose is a collective term. The most common type of polymers that belongs to the hemicellulose family of polysaccharides is xylan. Important aspects of the structure and composition of hemicellulose are the lack of crystalline structure mainly due to the highly branched structure, causing it to be amorphous (Kirk-Otmer, 2001). In contrast with lignin, hemicellulose is a polymer with acid insoluble character. By means of this, it is possible to conclude that the presence of acid highly improves the solubility of hemicellulose in water.

Cellulose is the most significant substance in wood as it determines the character of the fiber. Cellulose is a comparatively stable polymer, owing to the hydrogen bond network, which does not dissolve in common aqueous solvents and does not exhibit a melting point. In contrast with mineral fibers (glass, carbon fibers), the cellulose fibers have a good flexibility and elasticity, permitting them to sustain a high aspect ratio in the process of manufacturing (Hubbe et al., 2008). It provides mechanical strength and chemical stability to plants (Raven, Evert, & Eichhorn, 1992). The chemical formula of cellulose is $(C_6H_{10}O_5)_n$, whereby n is the number of repeating sugar units or the degree of polymerization (DP). The repeating unit in cellulose consists of two glucose molecules. The DP varies depending upon the cellulose source and the treatments it has received. DP for native cellulose is around 3500 whereas for most papermaking fibers, the DP lies between 600 and 1500. The properties of cellulose-containing materials are highly influenced by the DP of cellulose molecules (Smook, 1999). The structure of a unit chain of the polymer is disclosed in Figure 2-5.

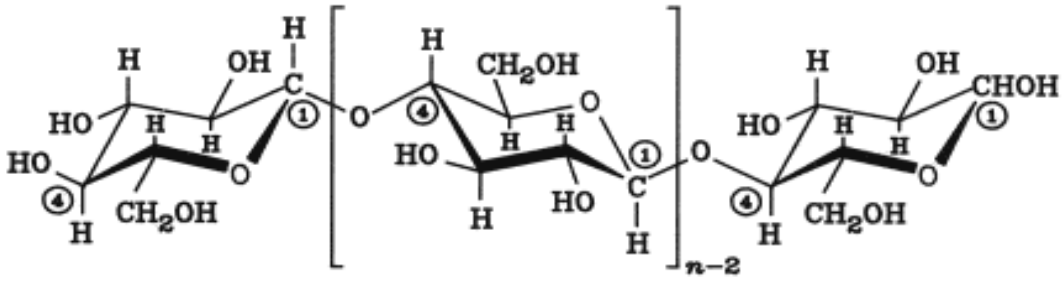

Figure 2-5: Structure of single cellulose molecule by Harmsen et al. (2010)

In alkaline solutions extensive swelling of cellulose takes place (Krassig & Schurz, 2002). Cellulose is believed to be insoluble in dilute acid solutions at low temperature. Nevertheless, its solubility increases at higher temperatures as the energy provided is sufficient to break the hydrogen bonds that hold the crystalline structure of the molecule (Harmsen et al., 2010). In higher plants such as wood, cellulose plays a vital role like reinforce element in the cell wall, generally together with lignin and hemicelluloses. These three polymers are closely associated with making up the lignocellulosic biomass. Literally, the lignocellulosic structure can be regarded as a bio-nanocomposite which results from a unique interplay between nano-scale domains of cellulose, hemicelluloses and lignin (Hon & Shiraishi, 2001).

Nanocellulose is a material composed of nano-sized cellulose fibrils with a high aspect ratio which is defined as the length to width ratio. Nanocelluloses can be derived from various renewable resources, such as wood, cotton, wheat straw and soy hulls, rice husk, pineapple leaf fibers and etc (Chen et al., 2011). However, the main raw material of this study is on wood resources which are rubberwood. The main purpose for the application of cellulose nanofibers in composite materials is due to the potentially high stiffness of cellulose fibers for reinforcement. Hubbe et al. (2008) added, the fact that practically any cellulose material could be considered as a potential source for isolation of nanocellulose structures denotes another key factor in using cellulose elements as reinforcing phase in polymeric matrix composites. This property can be achieved by breaking the structure of the plant in individualized nanofibers with high crystallinity via the reduction in amount of amorphous material. Chen et al. (2011) also added that the individualization of cellulose nanofibers from renewable resources has gained significant interest lately due to its astounding mechanical properties. Moreover, their exclusive morphology, chemical properties and low thermal expansion coefficient

increases its potential as reinforcement materials for nanocomposites. High surface area and the strong interaction of these celluloses with surrounding species such as water organic and polymeric compounds, nanoparticles and living cells, are the aftermaths of the nano-dimensions of the structural elements (Klemm et al., 2011). Advancing insight into the structural features and reactivity of cellulose has driven the step-by-step creation of brand-new types of materials (Huang et al., 2003).

2.4 Applications of nanocellulose

About 100 million tons per annum of commercially harvested cellulose is used for production of paper and paperboard (Ioelvich, 2008). The papermaking process embraces steps of preparing the paper components, wet refining, forming of wet sheet, pressing, drying, calendaring and finishing. Refining of cellulose fibers in water medium is the mandatory step in papermaking to obtain strong paper. Recent developments by Ioelvich and Leykin (2004) have shown the likelihood to increase the strength of paper with additive of nanocellulose particles to paper compositions. Such sheets exhibit admirable mechanical properties. These properties, according to Henriksson et al., 2008, is at least 2-5 times higher than that of common papers formed from conventional refining processes.

Nanocellulose can be used as a reinforcing filler to prepare composites with solutions of water-soluble polymers to modify the viscosity and increase mechanical properties of dry composites. The utmost importance has been the addition of nanocellulose to biodegradable polymers which permits both the improvement of mechanical properties and speeds up the rate of biodegradation (Ioelvich & Leykin, 2004).

Of late, nanocellulose has been called as the eyes of biomaterial highly applicable to biomedical industry. Pure nanocellulose is non-toxic for people and it is biocompatible. For that reason, it can be utilized for health care applications such as personal hygiene products, cosmetics and biomedicines. One of the modest applications of nanocellulose is the stabilization of medical suspensions against phase separation and sedimentation of heavy ingredients. Chemically modified cellulose can be a promising carrier for immobilization of enzymes and other drugs (Ioelvich & Figovsky, 2008a, b). Due to its nanosize, such a carrier-drug complex can penetrate through skin pores and treat skin diseases. Likewise, it can be used as a gentle but active peeling agent in cosmetics.